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Letter

Fabrication of laminated ZrC-SiC composite by vacuum hot-pressing sintering

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ABSTRACT

Laminated ZrC-SiC ceramic was prepared through tape casting and hot pressing. The green tapes of ZrC and SiC were prepared at room temperature. In order to improve the density of composite, the binder of green tapes were removed at 550 °C for 1 h. The laminated structure and the cracks propagation path, which is not a straight line, are observed by optical metalloscope. The compact laminated ZrC-SiC composite sintered by vacuum hot-pressing at 1650 °C for 90 min under pressure of 20 MPa was researched by X-ray diffraction and scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis. The results showed that interlayer bonding is tight, and no disordered phase has formed in the interlayers of ZrC or SiC, and the combination mode is physical mechanism.

1. Introduction

Ultra-high temperature ceramics (UHTCs), which belong to early transition metal borides and carbides, such as ZrC, ZrB_2, HfB_2 and HfC, are known for their ultra-high melting points (>3000 °C) [1]. In the family of materials, ZrC-based UHTCs have an unusual combination of properties, such as high temperature strength, as well as higher melting point, lower manufacturing costs, and more excellent thermal shock resistance compared with those of boride-based ceramics [2,3]. Despite possessing useful properties, the use of monolithic ZrC is highly limited because of its poor sintering ability and oxidation resistance. SiC is one of the most successful additives to improve both oxidation/ablation resistance and mechanical properties of UHTC [4]. Therefore, ZrC-SiC composite is a promising UHTC. ZrC and SiC have been investigated by several researchers, and various fabricating routes have been proposed [5–12].

Many researchers focus on processing and characterization of tough laminated ceramics and it has been increasing phenomenally. Laminates are beneficial materials because they are more convenient to produce compared with the fiber reinforced composites and the other bulk materials, the volume fraction of their components can be easily controlled, and they have generally superior mechanical properties [13]. As described in many reports, the laminated structure can improve the mechanical properties because it deflects cracks to enable the consumption of more fracture energy [14–16], which may be important for impact-resistant materials [17], high-temperature resistant exhaust gas filters, advanced micro-reactors, lightweight aeronautical materials, and tooling and wear components [18,19]. The presence of residual stresses at the surface of laminated composites can improve the wear resistance and the resistance to abrasive wear both under sliding and abrasive conditions [20,21]. At present, many laminated structural ceramics, such as Al_2O_3-ZrO_2, SiC-ZrB_2, Al_2O_3-Ti, Si_3N_4-BN and SiC-BN laminated ceramic composites, have been reported [22–26]. However, the studies on laminated ZrC-SiC ceramics are rare.

In the present study, the layered structures were introduced into the fabrication of the ZrC-SiC ceramics. The ZrC layers and SiC layers were fabricated through tap casting process, and then laminated ZrC-SiC composites were obtained via vacuum hot-pressing sintering technology with a uniaxial load. The different fracture mechanisms with brittle fractures were investigated with an optical metalloscope. The interfacial combination mode and elements of the sample were investigated through X-ray diffraction (XRD) and energy dispersive spectrometer (EDS). The morphology differences between ZrC layers and SiC layers were observed by scanning electron microscopy (SEM).

2. Experimental procedure

Commercially available ZrC powder (with mean particle size of 30 nm) and SiC powder (with mean particle size of 10 μm) were used as raw materials. And a small amount of CeO_2 (99.99% pure, from aladin) powders was used as sintering additives. The fabrication process of ZrC-SiC laminated ceramics was illustrated schematically in Fig. 1. First, the sol of 5 wt% PVB (Polyvinyl Butyral) and the plasticizing agent of 5 wt% PEG2000 (Polyethylene Glycol) were introduced in ethanol as adhesive and plasticizer. Then the

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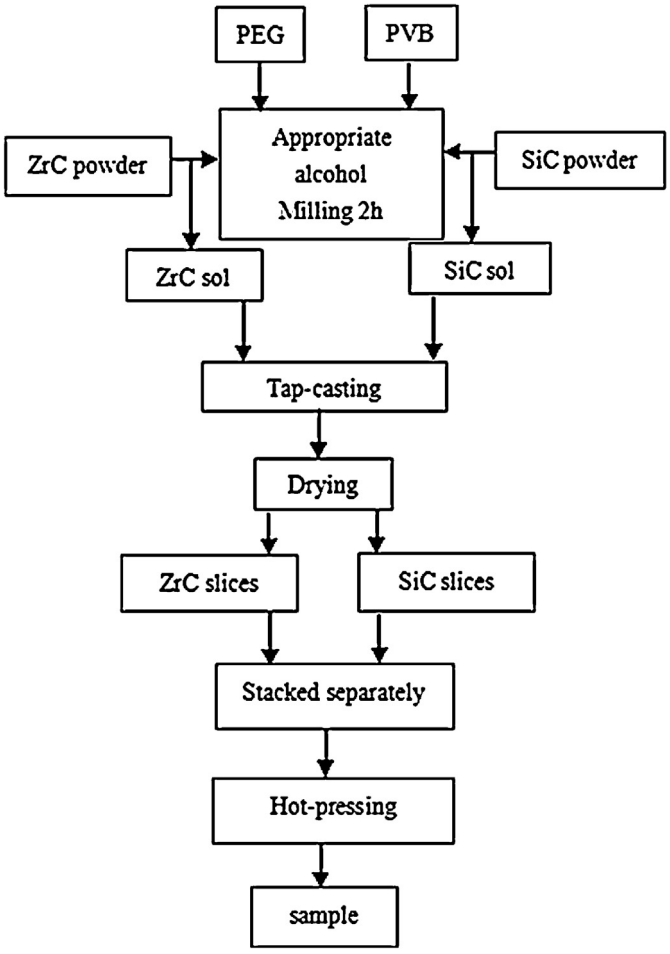

Fig. 1. Schematic diagram of preparation of laminated ZrC-SiC composite.

mixture was heated at 60 °C in a water bath until it was completely dissolved by ethanol. Secondly, 20 wt% ZrC powders, which weigh 15 g, and 0.2 wt% CeO_2, were mixed in the sol and dispersed through ultrasonication for 2 h. Third, the mixed sol was placed on a tape casting mold at room temperature for 4 h. The same steps were used with SiC and the quality of the SiC powder is 35 g. Afterward, the green gels were cut into slices (0.3 mm of thickness for SiC and 0.1 mm for ZrC). The ZrC sheets and SiC sheets were alternately stacked until the desired compositions were achieved. The stacked ZrC-SiC body, in which the number of SiC slices is 28 and the number of ZrC slices is 27, was placed in a graphite mold, heated to 550 °C at a heating rate of 10 °C/min, and then held for 60 min to remove the binder. Finally, the laminated sample was sintered in a vacuum hot-pressing furnace (VVPgr-80-2200, China) at 1650 °C for 90 min under an applied pressure of 20 MPa. After sintering, the quality of the whole composite is 40 g. There are some losses because of wear in the process of mold release.

The laminated structure of ZrC and SiC was observed with an optical metalloscope (BA310MET, China). The phases and compositions of interfaces were identified through XRD (D8-ADVANCE, Germany). The microstructure and diffusion distance of adjacent layers were analyzed via SEM (FEI QUANTA FEG 250, United States) with energy dispersive spectrometer (EDS).

3. Results and discussion

Fig. 2a shows the optical metalloscope graph of the side surface of the laminated ZrC-SiC sample, in which the dark layers are the ZrC interlayers and the gray layers are the SiC layers. The thickness of each SiC layer is about 400 μm and the thickness of each ZrC layer is 80 μm. The SiC and ZrC layers are distributed uniformly in the cross-section graph. Good combinations are observed every two layers, and the interface between them is not very straight because the material was pressed during sintering. According to the principle of Archimedes, the density of the sample is 3.02 g/cm^3 and the porosity of the sample is 9.3%.

Moreover, the microstructure of crack propagating paths and crack deflections of the laminated ZrC-SiC ceramic after fracture experiment is shown in Fig. 2b. The crack propagated downwards initially and then deflected into the ZrC layer when the ZrC-SiC interface was encountered. Afterward, the crack propagated horizontally within the ZrC layer. The crack turned back and propagated vertically again as the load further increased. This crack propagation and deflection were repeated at each ZrC layer, so vertical and horizontal cracks appeared alternately until the specimen finally fractured. As a result, the fracture was no longer a brittle fracture process but a layer-by-layer one, as shown in Fig. 2b. The crack deflection, which can extend crack propagation paths, can consume energy effectively. In a sense, the crack deflection can prevent the fracture of laminated ZrC-SiC ceramic.

Considering the coefficients of thermal expansion of the different materials they would have verified that the coefficients of thermal expansion of SiC are lower than that of ZrC, which have been detected that the coefficients of thermal expansion of SiC is 4.6×10^{-6} K^{-1} and the coefficients of thermal expansion of ZrC is 6.7×10^{-6} K^{-1} at room temperature. So according to the theory the SiC layer should be in compression while the ZrC layer should be in tension. In this experiment, the phenomenon is exactly the opposite. Because the particle size of SiC powder is large (particle size of 10 μm), the SiC layers are not fully dense structures. They have a higher porosity than the ZrC layers. Besides, the raw SiC sheets prepared through tape casting are thicker than ZrC sheets (0.3 mm of thickness for SiC and 0.1 mm for ZrC), which is the reason why

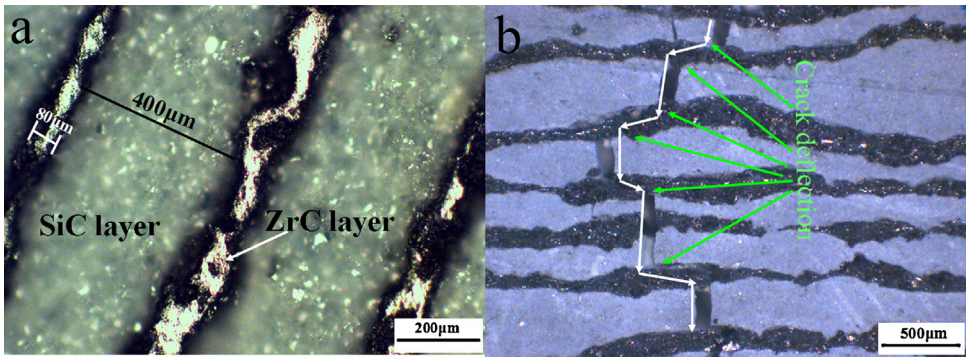

Fig. 2. Metalloscope micrograph of fracture surface of sample (a) and cracking propagation of ZrC-SiC laminated composite (b).

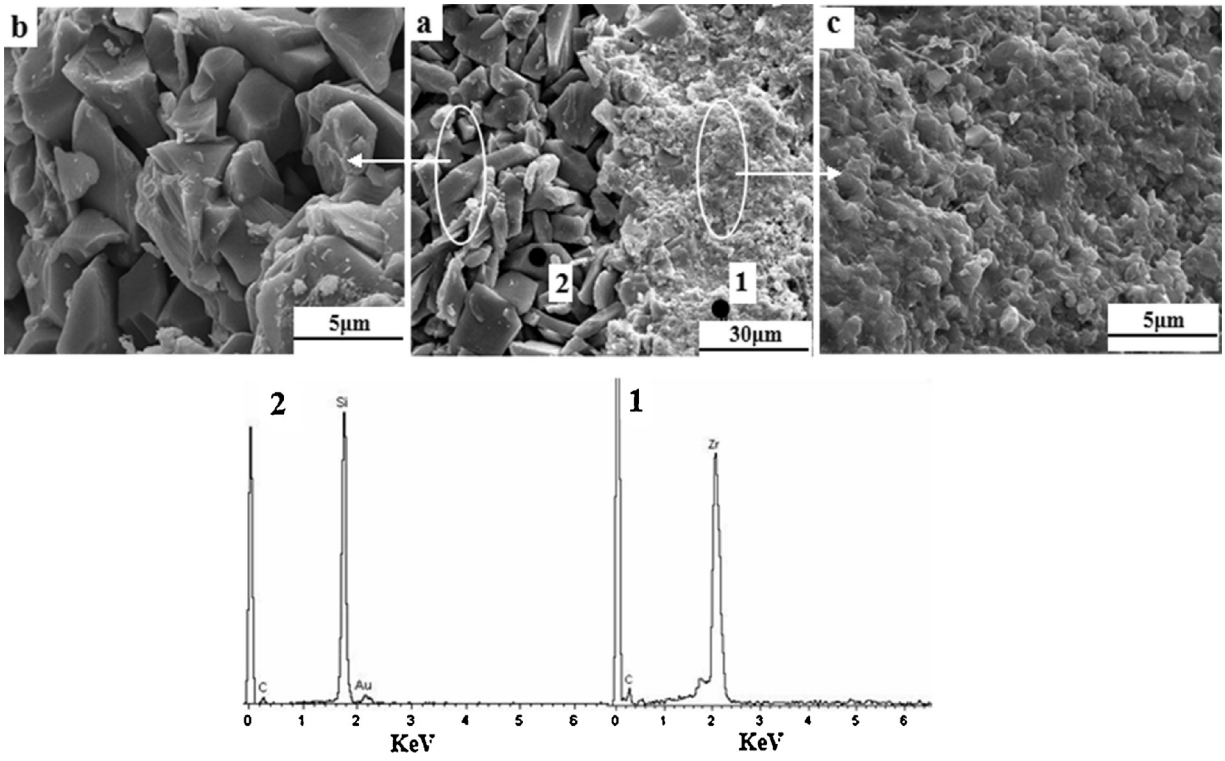

Fig. 3. SEM micrographs of interface between ZrC and SiC layers in composite and spot scan between ZrC and SiC layers, respectively.

ZrC layers are sintered more easily. Therefore, ZrC layers are denser than SiC layers. And the fracture could happen more easily in SiC layers.

Fig. 3 shows the microstructure of the fracture surface parallel to the hot-pressing direction in ZrC-SiC laminated ceramics with CeO_2 as sintering aids. Fig. 3a shows that the interfacial bonding is compact. The results from the enlarged images of Fig. 3b and Fig. 3c with EDS show that the loose layer is SiC and the compact one is ZrC. The SiC layer is loose because its particle size is larger than ZrC. The foregoing is also one of the reasons for SiC layers being thicker than ZrC layers. Fig. 3b clearly shows that the crystallinity of SiC is good, although it is a bit porous. Fig. 3c shows that the ZrC layer is compact because of hot-pressing sintering.

From the spot scan graphs in Fig. 3.1 and Fig. 3.2, the raw material with thicker layers are SiC and the raw material with thinner layers are ZrC. In conjunction with the XRD pattern of the sintered ZrC-SiC shown in Fig. 4, the phases of ZrC and SiC were identified, and did not react with each other to form any new phase during the sintering process. Thus, absolute ZrC phases and SiC phases existed in the interlayers of ZrC and SiC, respectively, indicating that no disordered phase has formed. These defined phases imply that the ZrC layers and SiC layers are well formed and that the combina-

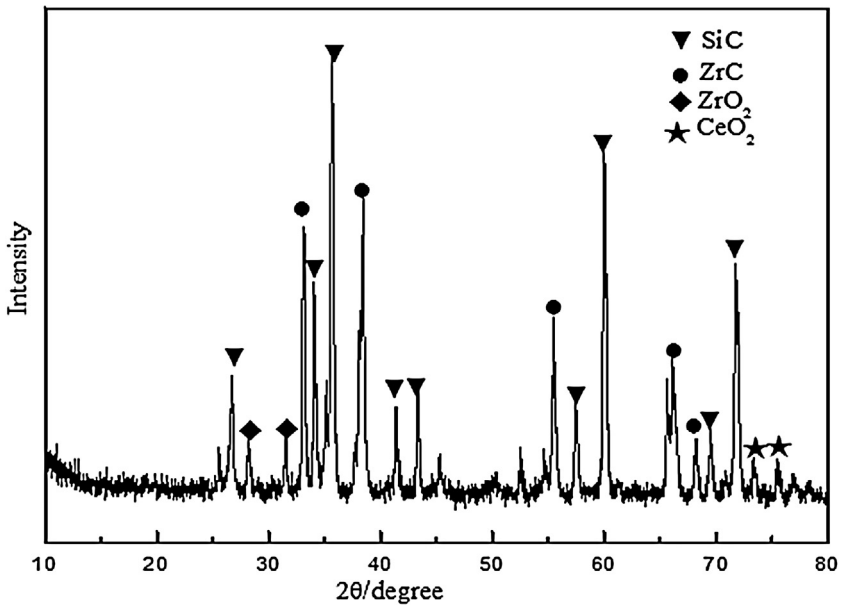

Fig. 4. XRD pattern of fracture surface of ZrC-SiC laminated composite.

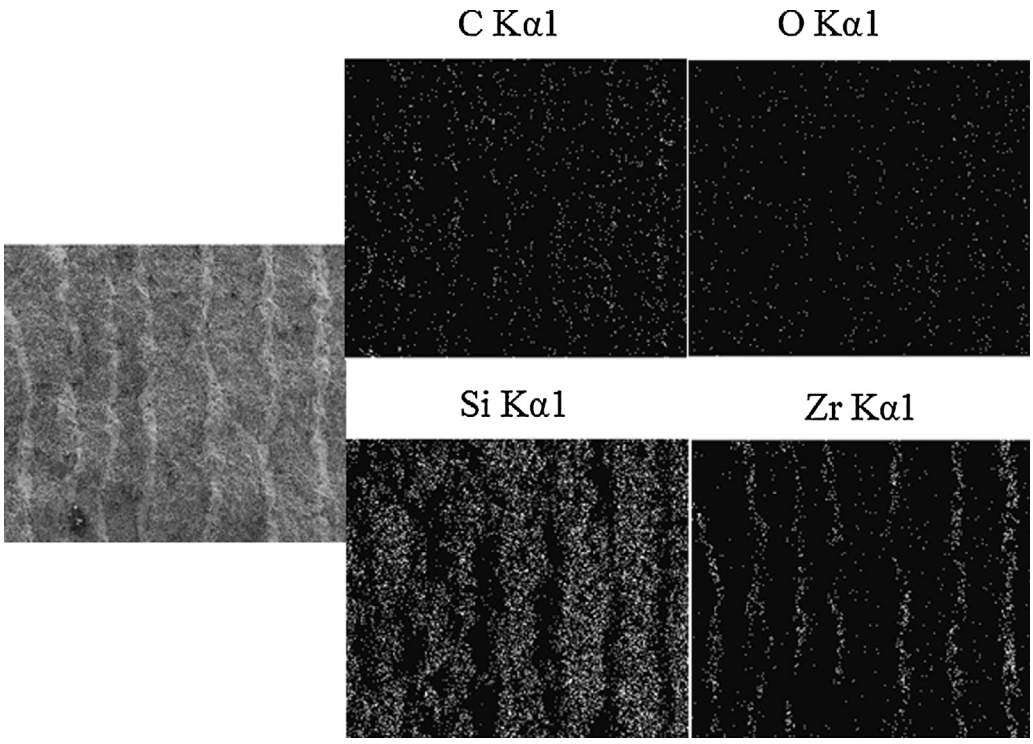

Fig. 5. EDX mapping for O, Si, Zr and C on the surface of ZrC-SiC laminated composite.

Table 1
Atomic percentage of all elements.

Element	C	O	Si	Zr	Au
Atomic percentage	24.49	1.23	46.87	26.52	0.88

tion mode of ZrC-SiC interface is physical. Distinct peaks of SiC and ZrC in the XRD pattern suggest that these substances comprise the main crystal phase. In addition, as shown in Fig. 4, small amounts of ZrO_2 and CeO_2 existed in the samples. The presence of ZrO_2 and CeO_2 in the sample is due to the raw material of ZrC powder that is too fine to be oxidized, and CeO_2 was used as sintering aid in the sintering process.

Fig. 5 shows the EDX mapping for O, Si, Zr and C on the polished surface of ZrC-SiC laminated composite. It can be seen that different phases consisting of Zr, O, Si and C are observed. The EDX mapping is consistent with the XRD pattern of fracture surface of the fabricated composite, as shown in Fig. 4. The Si and Zr mapping show that the ZrC-SiC laminated composite is prepared successfully. The same finding can be found in Fig. 2. The results also indicate that C and O are evenly distributed in the composite. Table 1 shows the atomic percentage of all elements. From Table 1, the composition still contains some oxygen. This may have two reasons: one is the oxidation of raw materials, and another is the introduction of CeO_2.

4. Conclusions

Laminated ZrC-SiC ceramics were prepared through tape casting and hot pressing according to the structure of natural biomaterials. Based on the optical metalloscope, the layers were clear and alternately stacked. The SEM micrograph showed that the laminated ZrC-SiC composite was sintered compactly through vacuum hot-pressing sintering with remarkable combination of different layers. Moreover, the combination mode of ZrC-SiC interface was physical. No reaction was noted between ZrC layers and SiC layers. Overall, the fabrication of laminated ZrC-SiC composite through vacuum hot-pressing sintering has been extremely successful. In addition, crack branches and deflections of interfaces prolong crack length and absorb more fracture strength.

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